

A silica-immobilized Pt²⁺ catalyst for the selective, aerobic oxidation of methane *via* an electron-transfer chain

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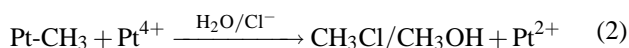
[Manuscript received January 5, 2008; revised March 7, 2008]

Abstract: The combination of Pt²⁺, benzoquinone and NaNO₂ forms an electron-transfer chain, which leads to the oxidation of methane by O₂ in CF₃COOH aqueous solution. The overall turnover number *per* hour (TOF) of methane at 120 °C is 0.5 h⁻¹, however, only about one fourth (23%) of methane is converted to the desired product of methanol in the formation of CF₃COOCH₃. The over-oxidation of methane to CO₂, over the catalyst with the Pt²⁺ species immobilized *via* 2,2'-bipyridyl as a ligand on the silica substrate, is depressed distinctly. Under the same conditions, the conversion to methanol dominates, and no CO₂ is observed, on account of the over-oxidation of methane, as confirmed by the isotope experiment.

Key words: methane; platinum; selective oxidation; electron-transfer chain

1. Introduction

The direct conversion of methane to methanol or methanol derivatives is of significant importance. Recent studies on metal-catalyzed systems in concentrated protonic acids, such as, H₂SO₄, CF₃SO₃H or CF₃COOH show that high selectivity can be obtained (>85%) under mild conditions (<250 °C) [1]. For example, Hg²⁺ and Pt²⁺ in H₂SO₄ exhibit a rather high activity using SO₃/H₂SO₄ as an oxidant [2,3]. We have previously found that the combination of three redox couples, that is, Pd²⁺/Pd⁰, benzoquinone(Q)/hydrobenzoquinone (H₂Q) and NO₂/NO, form an electron-transfer chain, which catalytically oxidizes methane to CF₃COOCH₃ in the presence of O₂ using CF₃COOH as a solvent [4]. Here we investigate the feasibility of extending this electron-transfer chain to other metals such as platinum, which has been initially studied by Shilov *et al.* [5]. In that process, methane had been oxidized to CH₃Cl, and CH₃OH catalyzed by PtCl₄²⁻ in liquid phase, in the presence of excess PtCl₆²⁻. PtCl₄²⁻ activates methane, and PtCl₆²⁻ acts as a stoichiometric oxidant as described in Equations (1) and (2) [5].



Although these tests on the activation and conversion of

methane using PtCl₄²⁻ as a catalyst in the aqueous solution of CF₃COOH, in the presence of excess PtCl₆²⁻, do yield CH₃Cl and CF₃COOCH₃ [6], but there is Pt⁰ precipitation. This will eventually result in the loss of activity because of the loss of active platinum species. One novel catalyst recently reported by Periana *et al.*, is dichloro(η-2-{2, 2'-bipyrimidyl}) platinum(II) [(bpym)PtCl₂], which catalyzes the formation of methyl bisulfate from methane in 102% H₂SO₄ and the TOF is 36 h⁻¹ at 220 °C. Although no Pt⁰ precipitate is reported in this process, the oxidant is SO₃ [3]. The use of O₂ as an oxidant is obviously preferred from the point of view of environmental protection. Although extensive efforts have been made to replace PtCl₆²⁻ with O₂ in the Shilov system, successful reports are very limited [7].

In addition, the separation and recovery of precious metal catalysts is difficult in these homogeneous catalytic reactions. This has often been alleviated using a heterogeneous catalyst, thus transforming a homogeneous reaction into a heterogeneous one [8]. Neumann *et al.* have studied methane conversion in the presence of O₂ by using a bipyrimidyl-platinum-polyoxometalate compound, which has been impregnated onto silica as a catalyst and they have observed the formation of CH₃OH, HCHO, and CH₃CHO, but the selectivity for CH₃OH is poor [7].

Here we choose a platinum complex dichloro(2,2'-bipyridyl)platinum(II) [simplified as (bipy)PtCl₂] as a catalyst, which is stable and also easy to obtain. We first investi-

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Foundation item: Ministry of Science and Technology of China (2005CB221405)

gate whether the combination of (bipy)PtCl₂, Q and NaNO₂ will also form an electron-transfer chain, which can catalyze the methane oxidation in the presence of O₂. On the basis of this finding, the immobilization of Pt²⁺ onto silica *via* chloropropylsilyl and 2,2'-bipyridyl as a ligand forming SiO₂-(bipy)PtCl₂, is studied. The reaction results show that methane is catalytically oxidized to CH₃OH during the formation of CF₃COOCH₃, in the presence of SiO₂-(bipy)PtCl₂, Q and NaNO₂.

2. Experimental

2.1. Chemicals and gases

The following chemicals were used as received: K₂PtCl₄, 2,2'-bipyridyl, 4,4'-dialkyl-2,2'-bipyridine (AR, Shanghai Chemical Co.); Q, NaNO₂, HCl (AR, Tianjin Kemiou); SiO₂ (AR, Qingdao Sea Chemical Co.); CF₃COOH (AR, Beijing Fine Chemical Co.); CH₄, O₂ (99.995%, Dalian Special Gases Co.); and the other chemicals were from Alfa Aesar (AR).

2.2. Preparation of catalysts

2.2.1. (bipy)PtCl₂ complex

(bipy)PtCl₂ was synthesized by boiling a mixture of K₂PtCl₄ and 2,2'-bipyridyl in 0.1 M HCl solution till a pale yellow precipitate appeared [9]. Then the mixture was filtrated and washed with distilled water, followed by drying at 100 °C for 2 h.

2.2.2. Immobilization of (bipy)PtCl₂ onto SiO₂ to obtain SiO₂-(bipy)PtCl₂

SiO₂ with a specific area of 319 m²/g was used as a support. We followed a reported procedure for SiO₂ functionalization with 4,4'-dialkyl-2,2'-bipyridine *via* chloropropylsilyl groups [10]. As shown in Figure 1, the chloropropylsilyl groups were first grafted to SiO₂. Then 4,4'-dialkyl-2,2'-bipyridine was added to the terminals of the chloropropylsilyl groups through an antichlorination reaction. Subsequently,

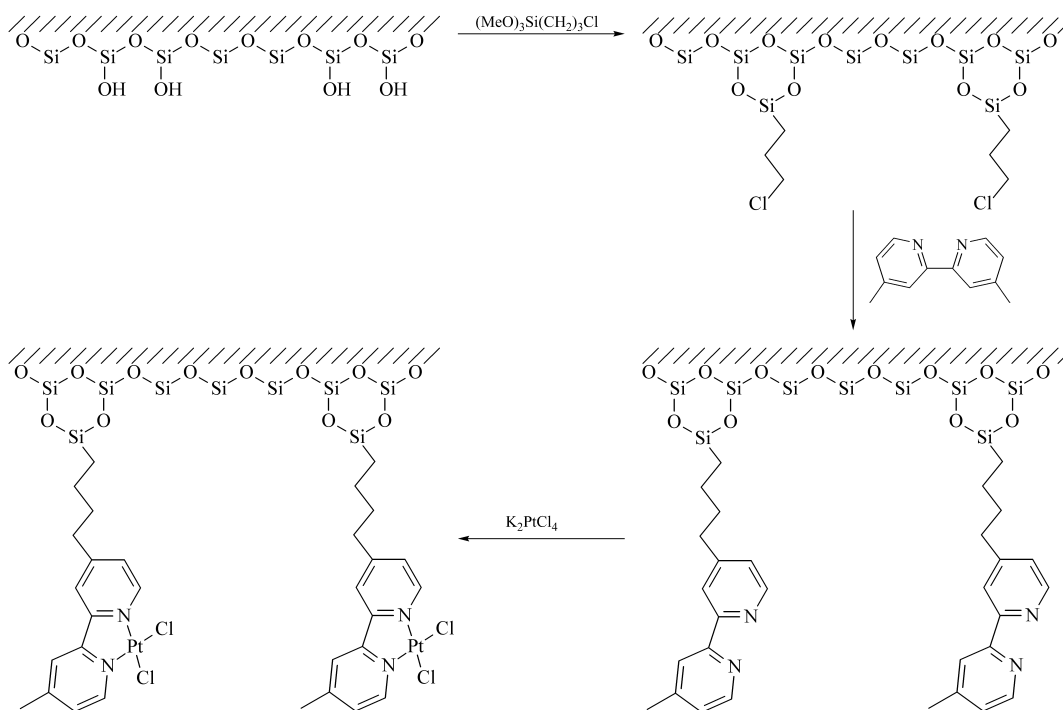


Figure 1. Synthesis procedure of SiO₂-(bipy)PtCl₂

2 g of functionalized SiO₂ was added into the K₂PtCl₄/HCl solution, which was obtained by dissolving 0.4 mmol K₂PtCl₄ in 20 ml HCl solution (0.1 M). The mixture was boiled for 5 h, followed by filtration. The remaining solid was washed with distilled water and then dried at 100 °C for 2 h. In this manner, the platinum catalyst was immobilized on SiO₂ and designated as SiO₂-(bipy)PtCl₂. The loading of Pt²⁺ in SiO₂-(bipy)PtCl₂ was determined by ICP (HWSB/F006–2005) at 27 °C.

2.3. Reaction tests

The catalysts and the solvent were mixed in a glass-liner, which was then sealed in a tailor-made autoclave. After the autoclave reactor had been purged with methane (30 atm) for three times, it was pressurized with reaction gases. The reaction mixture was heated to 120 °C and kept at that temperature for reaction, under continuous stirring with a magnetic stirrer. After the reaction, the reactor was cooled in ice water. The liq-

liquid and gas effluents were analyzed by GC (FULI 9790) with an FID (FFAP capillary column 15 m × 0.25 mm × 0.1 μm) and a TCD (Porapak QS 3 m × 3.00 mm × 2 mm or 5A molecular sieve 2 m × 3 mm × 2 mm). The analytical procedure used was the external reference method. Products were further confirmed by GC-MS (Agilent 6890 GC-5973 MS). The $^{13}\text{CO}_2/^{12}\text{CO}_2$ in the produced gases or air, that is the molar ratio of $^{13}\text{CO}_2$ to $^{12}\text{CO}_2$, was directly obtained from the ratio of the peak area of $^{13}\text{CO}_2$ ($m/z = 45$) to $^{12}\text{CO}_2$ ($m/z = 44$) in the GC-MS analysis. Turnover frequency (TOF) was expressed by the molar ratio of products to Pt^{2+} per hour in the reactions.

3. Results and discussion

3.1. Aerobic oxidation in the homogeneous system

In our previous study, it showed that Pd^{2+} first oxidized methane to $\text{CF}_3\text{COOCH}_3$ giving Pd^0 , which was not active for methane conversion. However, the presence of Q regenerated Pd^0 to Pd^{2+} and excess Q could prevent the precipitation of Pd^0 [4]. We first investigated whether Pt^0 precipitation could be prevented in the presence of excess Q and whether methane could be oxidized. The reactions were carried out in the absence of O_2 . Needless to say, Q had no effect on methane [4], and no oxidation was observed in the absence of $(\text{bipy})\text{PtCl}_2$. However, methane was converted to $\text{CF}_3\text{COOCH}_3$ in the presence of both $(\text{bipy})\text{PtCl}_2$ and Q, and the yield was related to the amount of H_2O in the reaction mixture as shown in Figure 2. With a total volume of CF_3COOH and H_2O at 3 ml, the yield of $\text{CF}_3\text{COOCH}_3$ increased to 17 μmol when CF_3COOH increased from 0 to 1.8 ml. The yield was reduced to 7 μmol with a further increase in CF_3COOH to 3 ml, until no water was present. This indicated that the optimal ratio of $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ was 1.8/1.2 (ml/ml). The molar ratio of the product $\text{CF}_3\text{COOCH}_3$ to the catalyst $(\text{bipy})\text{PtCl}_2$ was larger than 1, implying that the reaction became catalytic with respect to Pt^{2+} . In addition, no Pt^0 precipitate was observed after the reaction.

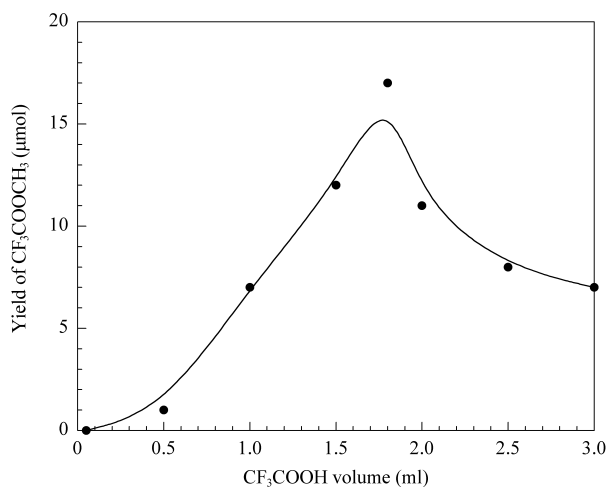


Figure 2. Effect of solvent on the reaction. Reaction conditions: $(\text{bipy})\text{PtCl}_2$ 15 μmol, Q 100 μmol, $\text{CF}_3\text{COOH} + \text{H}_2\text{O} = 3$ ml, CH_4 40 atm, 120 °C, 10 h

According to the reaction conditions as shown in Figure 3, ^{13}C NMR further analyzed the solid mixtures after reaction. The solvent was first removed by evaporation and the remaining substances were dissolved in DMSO-d_6 . Except the 2,2'-bipyridyl ligand (124.1, 127.7, 140.8, 148.4 and 156.7 ppm), H_2Q was detected (115.8 and 149.8 ppm), but no signal of Q was observed. These results implied that the combination of 15 μmol $(\text{bipy})\text{PtCl}_2$ and 20 μmol Q had oxidized methane to $\text{CF}_3\text{COOCH}_3$ and Q acted as a stoichiometric oxidant (Equation 3).

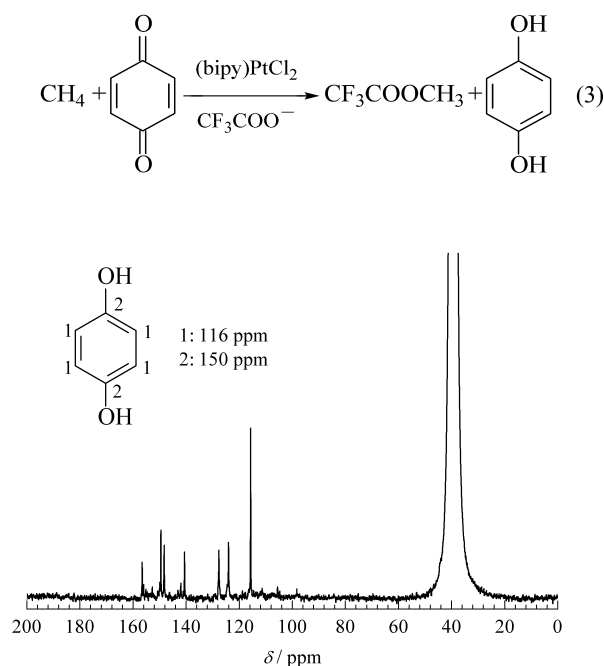


Figure 3. ^{13}C NMR spectra obtained in DMSO-d_6 after reaction. Reaction conditions: $(\text{bipy})\text{PtCl}_2$ 15 μmol, Q 20 μmol, CF_3COOH 1.8 ml, H_2O 1.2 ml, CH_4 40 atm, 120 °C, 10 h

In our previous study, NaNO_2 proved to be an efficient catalyst for conversion of H_2Q to Q in the presence of O_2 [4]. Therefore, we combined $(\text{bipy})\text{PtCl}_2$ (15 μmol), Q (20 μmol) and NaNO_2 (20 μmol) in the presence of 10 atm O_2 . The yield of $\text{CF}_3\text{COOCH}_3$ was coincidentally 17 μmol after reaction for 10 h. In addition, Figure 4 shows that the yield increased almost linearly versus the reaction time, within 15 h, and no Pt^0 precipitates were observed. This indicated that the combination of $(\text{bipy})\text{PtCl}_2$, Q and NaNO_2 also formed an electron-transfer chain and the selective, aerobic oxidation of methane to CH_3OH (in the format of $\text{CF}_3\text{COOCH}_3$) had been achieved. This process was similar to the Pd^{2+} system [4].

The origin of $\text{CF}_3\text{COOCH}_3$ has been confirmed by the isotope experiment, with 7 atm $^{13}\text{CH}_4$ (10% N_2) and 33 atm $^{12}\text{CH}_4$, and the reaction has been carried out under the same conditions. Except for $\text{CF}_3\text{COOCH}_3$ and CO_2 , no other products, such as CO, CH_3Cl , CH_3COOH , HCHO or CH_3CHO have been detected by GC-MS. For $\text{CF}_3\text{COOCH}_3$, the ratio of $\text{COO}^{13}\text{CH}_3$ ($m/z = 60$) to $\text{COO}^{12}\text{CH}_3$ ($m/z = 59$) fragments is 0.16, which is close to that of $^{13}\text{CH}_4/^{12}\text{CH}_4$,

implying that $\text{CF}_3\text{COOCH}_3$ is from methane. The GC-MS analysis for CO_2 in air shows the ratio of $^{13}\text{CO}_2$ ($m/z = 45$) to $^{12}\text{CO}_2$ ($m/z = 44$) is in the range of 0.033–0.043. However, under the same analytic conditions, $^{13}\text{CO}_2$ ($m/z = 45$)/ $^{12}\text{CO}_2$ ($m/z = 44$) = 0.075 for the produced CO_2 after reaction, which is clearly higher than the abundance of $^{13}\text{CO}_2$ in nature (0.033–0.043), indicating that there is a contribution of CO_2 from methane, which raises the concentration of $^{13}\text{CO}_2$.

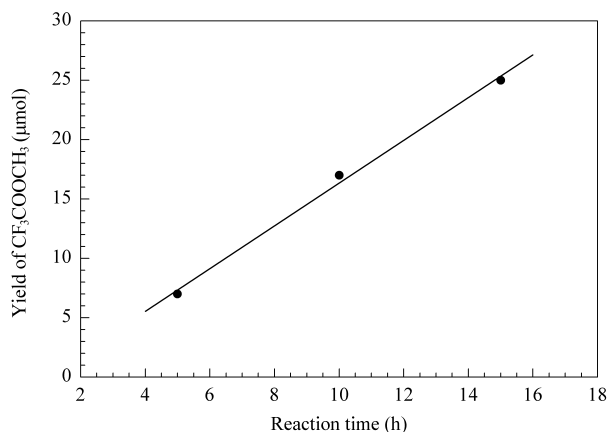


Figure 4. Yield of $\text{CF}_3\text{COOCH}_3$ versus the reaction time. Reaction conditions: (bipy)PtCl₂ 15 μmol , Q 20 μmol , NaNO₂ 20 μmol , CF_3COOH 1.8 ml, H₂O 1.2 ml, CH₄ 40 atm, O₂ 10 atm, 120 °C

The over-oxidation was further investigated by replacing all methane (run 1) by N₂ (run 2) in the reaction mixture, as shown in Table 1. In comparison to 200 μmol CO₂ detected in run 1, 143 μmol CO₂ was produced in run 2, which formed the oxidation product of CF_3COOH (run 2). As reported by Moiseev *et al.*, the CO₂ derived from CF_3COOH decarboxylation was also observed in the control experiment, which was not thought to be directly related to methane oxidation [11]. Thus, the amount of CO₂ produced from methane could be roughly estimated to be 57 μmol . In other words, the products from methane included 17 μmol $\text{CF}_3\text{COOCH}_3$ and 57 μmol CO₂. Thus the TOF was 0.5 h⁻¹, but the selectivity to $\text{CF}_3\text{COOCH}_3$ in this reaction was only 23%.

Table 1. Tests for over-oxidation over the (bipy)PtCl₂ system

Run	Gas (atm)	O ₂ (atm)	CO ₂ (μmol) ^a
1	CH ₄ (40)	10	200
2	N ₂ (40)	10	143

Reaction conditions: (bipy)PtCl₂ 15 μmol , Q 20 μmol , NaNO₂ 20 μmol , CF_3COOH 1.8 ml, H₂O 1.2 ml, 120 °C, 10 h. a: detected by GC

Although over-oxidation can be alleviated in a concentrated acid by forming a stable ester [1], it is still a challenge in dilute acid on account of ready hydrolysis of the ester to methanol. For example, when 500 μmol $\text{CF}_3\text{COOCH}_3$ is introduced into a solvent composed of 1.8 ml CF_3COOH and 1.2 ml H₂O, CH₃OH is observed by ¹H NMR, in addition to $\text{CF}_3\text{COOCH}_3$ (Figure 5). CH₃OH is not stable and easily oxidized to CO₂ under the reaction conditions.

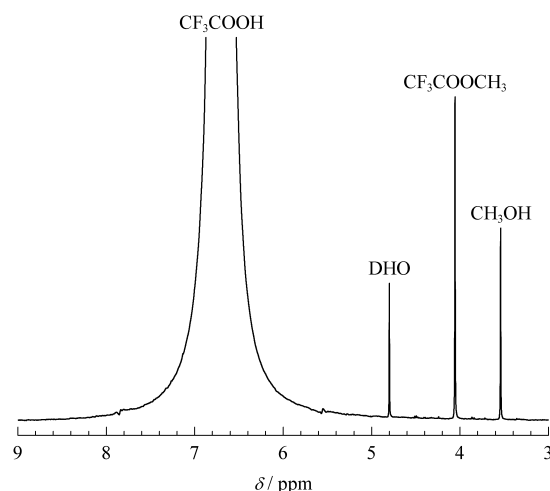


Figure 5. ¹H NMR of $\text{CF}_3\text{COOCH}_3$ in aqueous solution of CF_3COOH . Reaction conditions: $\text{CF}_3\text{COOCH}_3$ 500 μmol , CF_3COOH 1.8 ml, H₂O 1.2 ml, room temperature

3.2. Aerobic oxidation over the immobilized SiO₂-(bipy)PtCl₂ catalyst

In a further research, we studied methane conversion over the immobilized Pt²⁺ catalyst on SiO₂, and Pt²⁺ loading was 151 $\mu\text{mol}/\text{g}$. A reaction in the presence of 100 mg SiO₂-(bipy)PtCl₂ (equivalent to 15.1 μmol Pt²⁺), 20 μmol Q and 20 μmol NaNO₂ led to the formation of 19 μmol $\text{CF}_3\text{COOCH}_3$, indicating the validity of the catalytic effect of the electron-transfer chain, based on SiO₂-(bipy)PtCl₂. As shown in Figure 6, the yield of $\text{CF}_3\text{COOCH}_3$ increased with the amount of SiO₂-(bipy)PtCl₂ in the test range of 20–150 mg. At the same time, no Pt⁰ precipitates were observed even when the reaction time was 15 h.

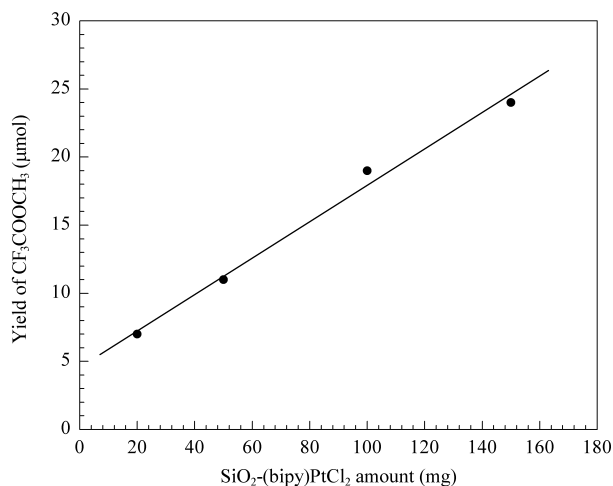


Figure 6. Yield of $\text{CF}_3\text{COOCH}_3$ versus SiO₂-(bipy)PtCl₂ amount. Reaction conditions: Q 20 μmol , NaNO₂ 20 μmol , CF_3COOH 1.8 ml, H₂O 1.2 ml, CH₄ 40 atm, O₂ 10 atm, 120 °C, 10 h

Again the isotope experiment (7 atm methane was replaced by ¹³CH₄) was carried out to confirm the origin of

CF₃COOCH₃ and the extent of over-oxidation. The ratio of COO¹³CH₃/COO¹²CH₃ = 0.19 was determined in the product, indicating that CF₃COOCH₃ was obtained from methane. The ratio of ¹³CO₂/¹²CO₂ was 0.029, which was very close to the natural abundance of ¹³CO₂. Therefore, the over-oxidation to CO₂ was negligible in contrast to the reaction before immobilization of the catalyst.

This is further confirmed by the parallel reactions of the SiO₂-(bipy)PtCl₂ catalyst and the results are listed in Table 2. In the presence of 40 atm CH₄, 155 μmol CO₂ is produced (run 1). After replacing methane with nitrogen, CO₂ is 145 μmol under the same reaction conditions (run 2). The amount of CO₂ in parallel reactions agrees within the accuracy of the our detection methods (~5%), therefore the over-oxidation can be neglected in such a heterogeneous system. Methane was selectively oxidized to CF₃COOCH₃, and TOF based on Pt²⁺ was 0.2 h⁻¹.

Table 2. Tests for over-oxidation over SiO₂-(bipy)PtCl₂ system

Run	Gas (atm)	O ₂ (atm)	CO ₂ (μmol) ^a
1	CH ₄ (40)	10	155
2	N ₂ (40)	10	145

Reaction conditions: SiO₂-(bipy)PtCl₂ 100 mg, Q 20 μmol, NaNO₂ 20 μmol, CF₃COOH 1.8 ml, H₂O 1.2 ml, 120 °C, 10 h. a: detected by GC

In the homogeneous system, the dissolved Pt²⁺ freely moves in the liquid, and its contact with methane has no limitation. However, once Pt²⁺ is immobilized onto the surface of silica, its movement is confined and the reaction takes place in a very thin liquid film, present in the interface of the solid catalyst and the solvent, so TOF decreases from 0.5 h⁻¹ to 0.2 h⁻¹. In general, over-oxidation of methane is severe in aqueous solution, but Neumann *et al.* also reported that no obvious over-oxidation was observed over a supported bipyrimidinylplatinum-polyoxometalate catalyst, even in water [7]. Though it is interesting that immobilization leads to a distinct depression of over-oxidation, no explanation can be given at present and further work is in progress. The catalyst separation and the recovery of platinum can be easily realized by simple filtration of the mixture, after reaction.

4. Conclusions

The combination of the metal complex of (bipy)PtCl₂ with Q and NO₂ forms an electron-transfer chain, which can catalyze the oxidation of methane in the presence of O₂ in the CF₃COOH aqueous solution at mild temperature, similar to Pd²⁺. The immobilization of the active Pt²⁺ species onto silica leads to a distinct depression of the over-oxidation of methane to CO₂. At 120 °C, the TOF of methane is 0.2 h⁻¹ in the presence of 100 mg SiO₂-(bipy)PtCl₂, 20 μmol Q, 20 μmol NaNO₂, 40 atm CH₄ and 10 atm O₂. To the best of our knowledge, it is the first example showing an immobilized metal catalyst using the chemical grafting method for the selective oxidation of methane to a methanol derivative.

References

- [1] Otsuka K, Wang Y. *Appl Catal A: General*, 2001, **222**: 145
- [2] Periana R A, Taube D J, Evitt E R, Löffler D G, Wentreck P R, Voss G, Masuda T. *Science*, 1993, **259**: 340
- [3] Periana R A, Taube D J, Gamble S, Taube H, Satoh T, Fujii H. *Science*, 1998, **280**: 560
- [4] An Z, Pan X, Liu X, Han X, Bao X. *J Am Chem Soc*, 2006, **128**(50): 16028
- [5] Geletii Y, Shilov A E. *Kinet Catal*, 1983, **24**: 413
- [6] Reaction conditions: 15 mol K₂PtCl₄, 100 mol H₂PtCl₆, 40 atm CH₄, 1.8 ml CF₃COOH, 1.2 ml H₂O, 120 °C, 10 h. The yield to CH₃Cl and CF₃COOCH₃ is 16 mol and 7 mol, respectively
- [7] Bar-Nahum I, Khenkin A M, Neumann R. *J Am Chem Soc*, 2004, **126**: 10236
- [8] Hancock R D, Howell I V, Pitkethly R C, Robinson P J. In *Catalysis: Heterogeneous and Homogeneous*, Proceedings of the International Symposium on the Relations between Heterogeneous and Homogeneous Catalytic Phenomena. Delmon B, Jannes G eds. Amsterdam: Elsevier, 1975. 361
- [9] Morgan G T, Burstall F H. *J Chem Soc*, 1934: 965
- [10] Nunes C D, Valente A A, Pillinger M, Fernandes A C, Romao C C, Rocha J, Goncalves I S. *J Mater Chem*, 2002, **12**: 1735
- [11] Vargaftik M N, Stolarov I P, Moiseev I I. *J Chem Soc, Chem Commun*, 1990: 1049